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1. Title of the Invention

Colored Flame Retardant Knitted Weave

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5. Attachments:

1) Specification	1
2) Copy of Application	1
3) Power of Attorney	1

SPECIFICATION

1. Title of the Invention

Colored Flame Retardant Knitted Weave

2. Claims

A flame retardant knitted weave with excellent light fastness, comprising a blend of 10 to 70 wt% aromatic polyamide fibers and 90 to 30 wt% non-thermoplastic fibers, and colored in such a way that measured color levels x, y, and z at a standard light, as stipulated in JIS-Z-8722, comply with the following:

$x \geq 0.25$
$y \geq 0.25$
$Z \leq 30$

3. Detailed Description of the Invention

The present invention relates to a flame retardant knitted weave with excellent light fastness, comprising a blend of aromatic polyamide fibers and non-thermoplastic fibers, and colored to a specific hue.

Aromatic polyamide fibers generally have an extremely high melting point and excellent weatherability, as well as a high electrical insulating properties, making them useful in a wide variety of applications, such as protective clothing and insulating sheets.

Although aromatic polyamide fibers thus enjoy many advantages, they shrink considerably, resulting in the formation of holes, when in direct contact with hot objects at 700 to 1000°C, for example. They also sometimes run the risk of igniting when used as protective clothing, for example. Other problems include discoloration (yellowing), high costs, and difficulties with dyeing under normal dyeing conditions.

The inventors undertook extensive research on the mixed spinning, weaving, knitting, and dyeing of various types of fibers, so as to gain a thorough understanding of such problems. As a result, they elucidated, in particular, changes in appearance caused

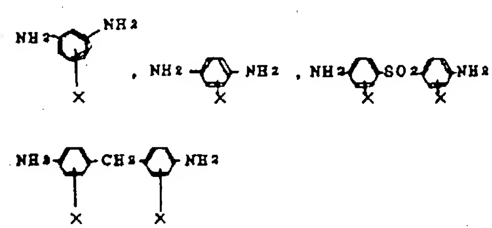
by yellowing caused by light, as well as the phenomena of shrinkage and hole formation occurring in woven materials at elevated temperatures.

That is, the present invention is a flame retardant knitted weave with excellent light fastness, comprising a blend of 10 to 70 wt% aromatic polyamide fibers and 90 to 30 wt% non-thermoplastic fibers, and colored in such a way that measured color levels x, y, and z at a standard light, as stipulated in JIS-Z-8722, comply with the following:

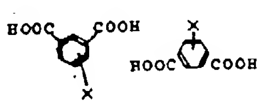
$x \geq 0.25$
$y \geq 0.25$
$Z \leq 30$

The present invention is described in further detail below.

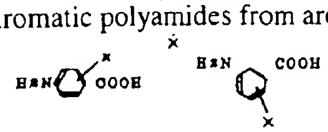
The flame retardant knitted weave in the present invention comprises aromatic polyamide fibers. Aromatic polyamide fibers can generally be produced from aromatic polyamides obtained by polycondensation of aromatic diamines and aromatic dicarboxylic acids. Examples of aromatic diamines include the following:



Examples of aromatic dicarboxylic acids include the following:



Aromatic polyamides from aromatic compounds such as the following may also be used:



The symbol × in these compounds represents a substituent such as a sulfonic acid group or halogen.

Examples of non-thermoplastic fibers contained along with the aromatic polyamide fibers in the flame retardant knitted weave include flame retardant fibers such as Novolak type phenol formalin resin fibers and regenerated cellulose fibers which have been rendered flame retardant. Fibers which are non-thermoplastic but are not flame retardant, such as regenerated cellulose fibers, cotton, hemp, wool, silk, and other such natural fibers, can be blended with the aromatic polyamide fibers to produce a knitted weave, which can then undergo a flame retardant process to render the non-thermoplastic fibers flame retardant.

The aromatic polyamide fibers and the non-thermoplastic fibers must be mixed spun into a blend in the present invention. The problems discussed above cannot be overcome by inter-heating, inter-weaving, or inter-knitting the fibers.

That is, the two fibers must be blended as uniformly as possible. Such uniform blending allows the two fibers to act synergistically.

Examples of mixed spinning include raw stock mixed spinning and draw mixed spinning, but the method is not particularly limited as long as a uniform blend is achieved.

The mixed spinning ratio is extremely important in the present invention. The aromatic polyamide fibers must be blended in an amount of 10 to 70 wt%. Less than 10 wt% compromises the inherent properties of the aromatic polyamide fiber, such as their heat resistance and mechanical strength. More than 70 wt%, on the other hand, will allow the heat resistance and mechanical strength of the aromatic polyamide fibers to be brought out, but the inherent yellowing tendency of aromatic polyamide fibers will make it difficult to obtain a colored knitted weave with better apparent light fastness. The mixed spinning ratio of the aromatic polyamide fibers is preferably in the range of 30 to 65 wt%.

A variety of methods may be employed to color the knitted weave blended within the aforementioned mixed spinning ratio. The following are examples.

1. The aromatic polyamide fibers are mixed spun with non-thermoplastic fibers, and only one of either of the fibers is colored in the form of yarn or a knitted weave.

2. The aromatic polyamide fibers or non-thermoplastic fibers are pre-dyed, and the fibers are then mixed spun.

3. The aromatic polyamide fibers and non-thermoplastic fibers are mixed spun, and both fibers are dyed in the form of yarn or a knitted weave.

4. The aromatic polyamide fibers and non-thermoplastic fibers are pre-dyed and then mixed spun.

Although such methods can be adopted, it is generally more advantageous to dye only the non-thermoplastic fibers when the mixed spun non-thermoplastic fibers are readily dyed, because aromatic polyamide fibers are more difficult to dye under ordinary conditions. Furthermore, as will be described below, there is less "flickering" and better light fastness when the fibers are mixed spun and only one of the fibers is dyed to the hues in the range of the present invention.

Of course, when the aromatic polyamide fibers are readily dyed, both fibers may be dyed, as noted above, or the aromatic polyamide fibers alone may be dyed. In either case, at least one of the fibers must be dyed.

The hues of the knitted weave in the present invention are determined in accordance with JIS-Z-8722. That is, the fibers are limited to being colored in such a way that x and y of the three color coefficients x, y, and z, which are calculated from three stimulus values X, Y, and Z measured at a standard light C, are each at least 0.25, and Z of the three stimulus values is no more than 30%. The dyes and dyeing methods which can be used are limited only to the extent that the hues are within this range. That is, commonly used dyes and methods may be used.

Outside the aforementioned range of hues, the aromatic polyamide fibers will undergo considerable yellowing, no matter what dye or method is used, so that the apparent light fastness of the knitted weave will be no more than a grade of 3, making it unusable for practical purposes. The correlation between the hue and light fastness is describe in further detail in the examples below.

The colored knitted weave in the present invention must be flame retardant as a whole. Although the object of the present invention can be achieved without further modification of the knitted weave of such a blend of aromatic polyamide fibers and flame retardant non-thermoplastic fibers, a flame retardant process is required after the knitted weave has been produced when the blend comprises aromatic polyamide fibers and non-fame retardant non-thermoplastic fibers.

A common flame retardant agent can be used in cases containing natural fibers such as cellulose fibers, for example. Specific examples include inorganic compounds such as ammonium phosphate, borax, phosphoric acid, and ammonium salts of halogen compounds; and organic compounds such as tetrakis hydroxymethyl phosphonium chloride and derivatives thereof, trisaziridinyl phosphine oxide and derivatives thereof, polyaminophosphates, tris halogenated alkyl phosphates, bisphenol halides, halohydrocarbons, polyphosphate amides, and polyphosphonitriles. The flame retardant agent is applied as uniformly as possible to the knitted weave by a method such as dipping, pad drying, spraying, or coating. To provide flame retardant properties sufficient for protective clothing, the initial flame retardant properties should, of course, be exceptional, and the flame retardant agent should not fall off as a result of dry cleaning or when washed with water. For that reason, the use of flame retardant agents that react with the fibers is preferred. Although the level of initial flame retardance will vary depending on the application or the like, the lowest oxygen index (LOI) (the minimum amount of oxygen needed for samples to continue burning in a mixed gas atmosphere of oxygen and nitrogen, as determined in ASTM D-2863-70; greater numerical values indicate better flame retardance) should be at least 25.

The knitted weave of the present invention has the following advantages.

1. The LOI is higher than when aromatic polyamide fibers are used alone or when flame retardant non-thermoplastic fibers are used alone.

2. There is virtually no shrinkage when in direct contact with hot objects, while the strength of the portion of the knitted weave that is in contact lasts longer.

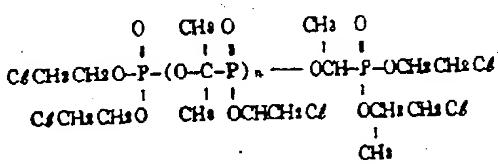
3. The apparent light fastness is better, with a grade of 4 or 5, or even higher.

4. The knitted weave is less expensive than 100% aromatic polyamide fiber products.

The colored flame retardant knitted weave of the present invention allows the inherent strengths of aromatic polyamide fibers to be fully exploited, while avoiding the drawbacks associated therewith. The excellent performance allows the invention to be used in a wide range of applications such as protective clothing.

Example 1

Two-ply yarn with a yarn count of 20 was produced by raw stock mixed spinning of 45 wt% aromatic polyamide fibers (2 d, 51 mm) consisting of a polymetaphenylene isophthalamide synthesized from metaphenylene diamine and isophthaloyl chloride, and 55 wt% viscose regenerated cellulose fibers (2 d, 51 mm) containing 25 wt% (relative to cellulose) compound having the following structure:



This yarn was used to produce a 2/2 knitted woven material (basis weight of 250 g/m^2).

The material was then scoured in the usual manner. The LOI (ASTM D-2863-70) of the material was 35. This was a considerably high value compared to the value of 26 for woven material comprising flame retardant regenerated cellulose fiber alone and the value of 32 for woven material comprising poly(metaphenylene isophthalamide) fibers alone. The blended weave was then dyed to varying hues with combinations of the following reactive dyes (all by Mitsubishi Kasei Kogyo).

Diamila	Yellow GR	a%	omf
Diamila	Red BB	b%	omf
Diamila	Brilliant Blue B	c%	omf

The dyeing conditions are outlined below.

Dye (a + b + c)	2% omf
Sodium sulfate	60 g /L
Sodium carbonate	20 g/L

60°C × 60 min.

Table 1 shows the correlation between the light fastness (JIS L-1044) and the three color coefficients as well as the Z value when materials were dyed with varying dye concentrations. Nos. 1 through 17 are products of the invention. All others are comparative examples.

Under the aforementioned dyeing conditions, the aromatic polyamide fibers were not dyed; only the regenerated cellulose was dyed. In the table, A, B, and C indicate dyed woven materials containing no aromatic polyamide fibers. Table 1 shows that Product Nos. 1 through 17 of the invention all had a light fastness of grade 4 or better, with an excellent appearance (in terms of flickering).

Undyed fabrics completely yellowed when exposed to light because the aromatic polyamide fibers were discolored by the light, resulting in a light fastness of no more than grade 3, which was unsuitable for clothing.

Table 1

No.	a%	b%	c%	x	y	Z (%)	light fastness (grade)	flickering
1	20	--	--	0.454	0.440	13.0	4 to 5	none
2	1.6	0.4	--	0.496	0.354	12.5.00 13.5	5	none
3	1.6	--	0.4	0.372	0.432	13.0	4 to 5	none
4	1.2	0.8	--	0.496	0.333	13.8	4 to 5	none
5	1.2	0.4	0.4	0.388	0.356	14.6	4 to 5	low
6	1.2	--	0.8	0.334	0.410	14.0	4 to 5	low
7	0.8	1.2	--	0.490	0.316	15.0	4 to 5	low
8	0.8	0.8	0.4	0.381	0.327	15.0	4 to 5	low
9	0.8	0.4	0.8	0.358	0.303	16.0	4 to 5	low
10	0.8	--	1.2	0.306	0.378	16.3	4	low
11	0.4	1.6	--	0.466	0.304	17.0	4	low
12	0.4	1.2	0.4	0.370	0.298	18.0	4	low
13	0.4	0.8	0.8	0.330	0.298	19.0	4	low
14	0.4	0.4	1.2	0.304	0.308	21.6	4 to 5	low
15	0.4	--	1.6	0.281	0.338	21.0	4	low
16	--	2.0	--	0.446	0.271	23.1	4	low to med
17	--	1.6	0.4	0.344	0.255	25.0	4	low to med
18	--	1.2	0.8	0.305	0.243	27.3	≤ 3	high
19	--	0.8	1.2	0.281	0.245	31.0	≤ 3	high
20	--	0.4	1.6	0.261	0.239	37.6	≤ 3	high
21	--	--	2.0	0.234	0.241	40.1	≤ 3	high
A	--	--	2.0	0.229	0.250	11.5	5	none
B	2.0	--	--	0.460	0.450	22.0	5	none
C	--	2.0	--	0.450	0.280		5	none
Undyed fabric				0.328	0.356	69.0	≤ 3	--

Example 2

Two-ply yarn with a yarn count of 30 was produced by raw stock mixed spinning of 40 wt% cotton and 60 wt% aromatic polyamide fibers (2 d, 51 mm) synthesized from metaphenylene diamine and isophthaloyl chloride. The yarn was then used to produce a plain weave (basis weight of 200 g/m^2). The material was then scoured in the usual manner, and the same dyes used in Example 1 were used to dye the material to the hues given in Table 2.

dye assistant

Dimethyl phosphate carboxymethylol amide 20%

$$\left(\begin{matrix}CH_3O\\CH_3O\end{matrix}\right)\!\!>\underset{\underset{O}{\|}}{P}-CH_2CH_2\underset{\underset{O}{\|}}{C}-NHCH_2OH$$

Hexamethylol melamine	7%
Ammonium chloride	0.5%
Water	balance

The materials were dipped in baths having the above composition, were wrung at a pick up of 100%, were dried for 2 minutes at 100°C, and were heat treated for 5 minutes at 160°C. The LOI was 36.

The LOI of a woven material consisting only of aromatic polyamide fibers was 32. The LOI of 100% cotton prepared under the aforementioned conditions was 27. Table 2 gives the light fastness.

Table 2

	x	y	Z	light fastness (grade)	Flickering
Product of invention	0.40	0.42	19.0	5	none
Product of invention	0.39	0.41	24.0	5	none
Comparative product	0.38	0.42	57.0	≤ 3	none
Comparative product	0.24	0.27	39.0	≤ 3	high
(Undyed fabric)	0.33	0.36	71.0	≤ 3	none

Table 2 shows that the products of the invention all had good light fastness, with an attractive appearance (no flickering).

Example 3

The woven material obtained in Example 1 was held horizontal, and a match was placed in direct contact therewith. The material turned a blackish brown but did not shrink as a result of the heat. The burned part also did not tear when manually rubbed, indicating considerable strength and flexibility.

In similar evaluations of material consisting of 100% aromatic polyamide fibers, the part in contact with the flame shrank and hardened, so that holes readily formed when manually rubbed.

Material made of flame-retardant regenerated cellulose fibers alone also resulted in the formation of holes when manually rubbed in the same manner.

6. Other Inventors

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